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Preparation and Characterization of Monomeric and Dimeric Group IV Metallocene Dihydrides Having Alkyl-Substituted Cyclopentadienyl Ligands

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A series of zirconocene dihydride complexes of the general form $[(R_nCp)_2ZrH_2]_x$ having substituted cyclopentadienyl ligands has been prepared by hydrogenation of the corresponding dimethyl complexes. The most sterically crowded members ($Cp^*(\eta^5\text{-}C_5HMe_4)ZrH_2$, ($Cp^*$ = (η^5-C_5Me_5)), $Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}ZrH_2$ and $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrH_2$) are monomeric; those less crowded members ($[Cp^*\{\eta^5\text{-}C_5H_4(CMe_3)\}ZrH_2]_2$, $[Cp^*(THI)ZrH_2]_2$ (THI = η^5-tetrahydroindenyl), and $[\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}_2ZrH_2]_2$) are predominantly dimeric in benzene solution. $Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}ZrH_2$ and $(\eta^5\text{-}C_5HMe_4)_2ZrH_2$ exist as equilibrium mixtures of monomer and dimer in benzene solution. The hydride ligands rapidly exchange with D_2, affording the dideuteride complexes. Deuterium incorporation into some of the substituents on the cyclopentadienyl rings of the monomeric dihydride complexes is also observed. The X-ray structures of $Cp^*_2HfH_2$, $Cp^*\{\eta^5\text{-}C_5H_4(CMe_3)\}ZrCl_2$, $Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}ZrCl_2$ and $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrCl_2$ are reported.

Introduction

Transition-metal hydrides constitute an important class of compounds because of their prevalence in both catalytic and stoichiometric processes.[1] Hydride complexes of group IV metallocenes have been implicated as catalysts and as important intermediates in olefin hydrogenation[2] and polymerization reactions.[3] Despite their widespread utility, the molecularity and structures of zirconocene and hafnocene dihydrides have not been systematically investigated.

Early reports of zirconocene dihydride complexes concern the preparation of simple alkyl substituted bis(cyclopentadienyl) complexes of the general form $\{(\eta^5\text{-}C_5H_4R)_2ZrH_2\}_n$ (R = H, Me, $CHMe_2$, CMe_3; $n \geq 2$), obtained via hydrogenation of the corresponding dimethyl complexes at elevated temperature (80 °C) and pressure (60 atm).[4] Bis(tetrahydroindenyl)zirconium dihydride dimer has also been prepared via hydrogenation of the corresponding bis(indenyl)zirconium dimethyl complex as a result of hydrogenation of both of the zirconium methyl bonds as well as the benzo groups of the indenyl ligands.[5] Zirconocene dihydrides $[(\eta^5\text{-}C_5H_4CMe_3)_2ZrH_2]_2$ and $[(\eta^5\text{-}C_5H_4SiMe_3)_2ZrH_2]_2$ have been prepared via an alternate route, reduction of metallocene dichloride complexes with borohydride or aluminohydride reagents.[6,7]

More recently, *ansa*-zirconocene dihydride complexes have been synthesized. Buchwald[8] has reported the synthesis of $[rac\text{-}(EBTHI)MH_2]_2$ (EBTHI = ethylene-1,2-bis(η^5-tetrahydroindenyl); M = Zr, Hf) via reduction of the corresponding dichloride complexes with $NaBEt_3H$. Royo[9] has used similar methodology to prepare dimeric, doubly $SiMe_2$-bridged $[(Me_2Si)_2(\eta^5\text{-}C_5H_3)_2MH_2]_2$ (M = Zr, Hf). Parkin has prepared $[OpZrH_2]_2$ (Op = $Me_2Si(\eta^5\text{-}C_5Me_4)_2$) via hydrogenation of the dimethyl complex at elevated temperatures in cyclohexane solution.[10] In all cases, stable dimeric zirconocene dihydrides resulted, with no reports of detectable amounts of the monomer in solution, although facile interconversion of $[OpZrH_2]_2$ with the monomer was implicated by its variable temperature ^1H NMR behavior.[10]

Very few monomeric zirconocene and hafnocene dihydride complexes have been prepared and isolated. Like their group 3 counterparts,[11] most group IV metallocene hydride complexes are subject to dimerization through formation of relatively robust three-center, two-electron hydride bridges. In fact, to our knowledge, the only monomeric zirconocene and hafnocene dihydride complexes prepared to date are those employing two bulky pentamethylcyclopentadienyl (Cp*) ligands, Cp^*_2-

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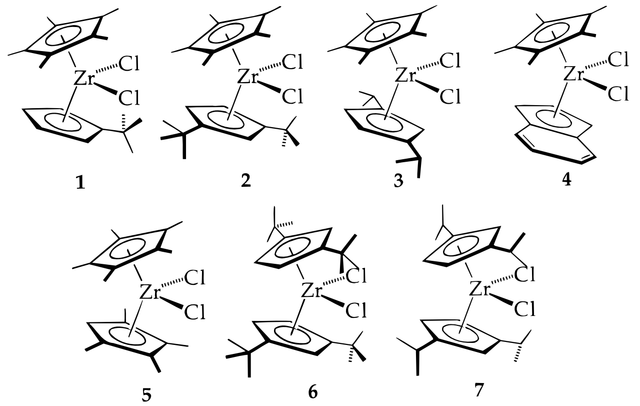
Scheme 1



MH_2.[12] Elucidation of the effects of ligand array on the position of the monomer−dimer equilibrium has not been established. In this report, we describe the preparation and solution behavior of a variety of new zirconocene dihydride complexes and through this study explore some of the factors that govern the monomer−dimer equilibrium. The H/D exchange reactions of these hydride complexes with deuterium are described. We also present the results of X-ray crystal structure determinations for monomeric $Cp^*_2HfH_2$, together with some representative precursors, $Cp^*\{\eta^5\text{-}C_5H_4(CMe_3)\}ZrCl_2$, $Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}ZrCl_2$, and $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrCl_2$.

Results and Discussion

Synthesis and Solution Behavior of Zirconocene Dihydrides. Preparations of "mixed ring" zirconocene dichloride complexes have been carried out in a straightforward manner by addition of the corresponding lithiocyclopentadienide to readily available Cp^*ZrCl_3.[13] Thus, $Cp^*\{\eta^5\text{-}C_5H_4(CMe_3)\}ZrCl_2$[14] (**1**), $Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}ZrCl_2$ (**2**), $Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}ZrCl_2$ (**3**), $Cp^*(Ind)ZrCl_2$ (**4**) (Ind = $(\eta^5\text{-}C_9H_7)$), and $Cp^*(\eta^5\text{-}C_5HMe_4)ZrCl_2$ (**5**) have been prepared in yields ranging from 60% to 83%. Additionally, $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrCl_2$ (**6**) and $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}_2ZrCl_2$ (**7**) (Scheme 1) have been obtained in moderate yield from the reaction of 2 equiv of the lithiocyclopentadienide with $ZrCl_4$ in refluxing toluene. All of the dichloride complexes are air stable and can be purified either by recrystallization or sublimation at 140 °C (10^{-4} Torr).

Single crystals of **1**, **3**, and **6** were obtained from toluene solution and their structures were established by X-ray diffraction. As shown in Figures 1−3, the cyclopentadienyl substituents arrange themselves to avoid both the narrow ("back") portion of the zirconocene wedge and the large chloride ligands. Thus, the *tert*-butyl substituent of **1** is situated slightly off the center of the wedge with CMe_3 methyl groups arranged to minimize interactions with the cyclopentadienyl CHs and the chloride ligands. The isopropyl groups for **3** are lateral, related by a mirror plane that bisects the Cl−Zr−Cl plane, with one C−CH_3 bond oriented perpendicular to the cyclopentadienyl plane and the other directed into the wedge away from the chlorine atom. The four *tert*-butyl groups for **6** are pairwise related by a crystallographic 2-fold symmetry axis that bisects the Cl−Zr−Cl angle.

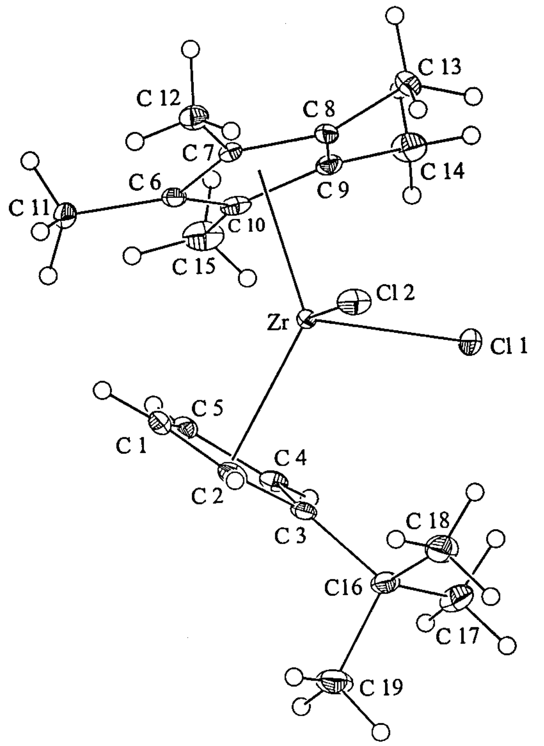


Figure 1. Molecular structure of **1** with selected atoms labeled (50% probability ellipsoids).

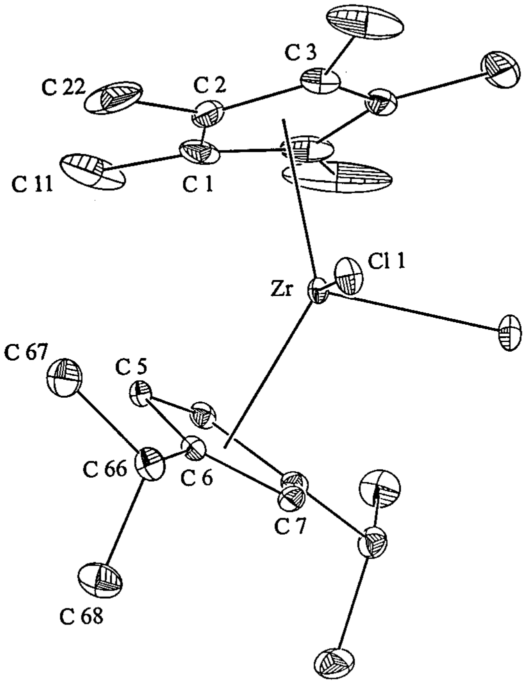


Figure 2. Molecular structure of **3** with selected atoms labeled (50% probability ellipsoids; hydrogen atoms omitted for clarity).

During the course of our investigations, we have obtained X-ray quality crystals of $Cp^*_2HfH_2$, which has

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(12) (a) Manriquez, J.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. (b) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

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(14) This compound has been reported previously: Vanderheijen, H.; Hessen, B.; Orpen, A. G. *J. Am. Chem. Soc.* **1998**, *120*, 1112.

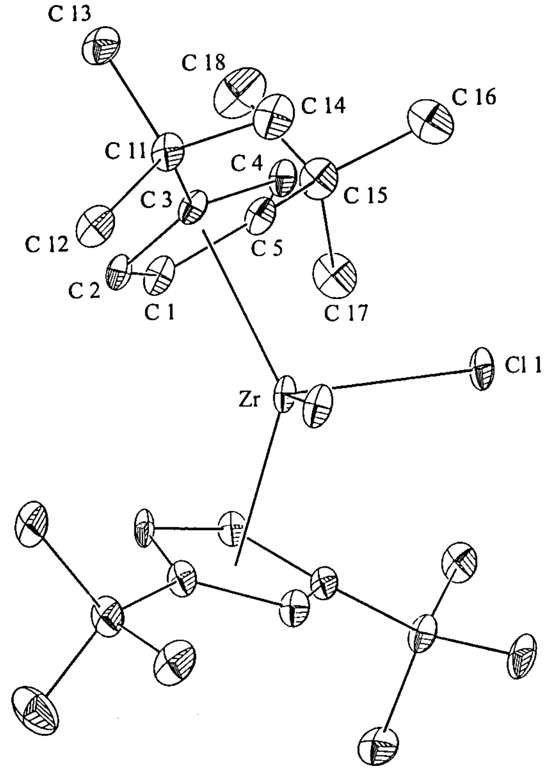
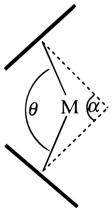


Figure 3. Molecular structure of **6** with selected atoms labeled (50% probability ellipsoids; hydrogen atoms omitted for clarity).

been prepared via reduction of the dichloride complex with 2 equiv of *n*-BuLi under an atmosphere of dihydrogen.[12b] To our knowledge, this is the first monomeric group IV metallocene dihydride to be characterized crystallographically. The crystals obtained for the diffraction experiment were twinned, and as a result location of the hydride ligands was not possible. Despite the complications of crystal twinning, we are confident that the structure is indeed the monomeric dihydride as shown in Figure 4. It is noteworthy that, presumably as a result of the small size of the hydride ligands, the two η^5-C_5Me_5 ligands assume a very "closed" metallocene structure. As can be seen from the data in Table 1, the centroid−Hf−centroid ($\theta = 144.1(2)°$ and 145.0(2)°) and cyclopentadienyl normal−cyclopentadienyl normal ($\alpha = 145.2(2)°$ and 145.9(2)°) angles for the two independent molecules in the unit cell are much larger than those for **1**, **3**, **6**, or other hafnocene dichloride complexes that have been structurally characterized ($\theta = 129-131°$; $\alpha =$ ca. 121−128°). Chloride ligands thus exert an unfavorable steric repulsion on those ring carbons most out of the metallocene wedge, resulting in smaller values for θ and α and larger differences between these two angles.

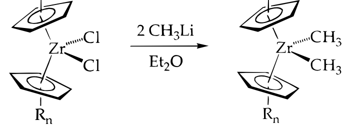
Table 1. Centroid-M-Centroid (θ) and Cyclopentadienyl Normal−Cyclopentadienyl Normal (α) Angles for $Cp^*_2HfH_2$, 1, 3, 6, and Related Hafnocene Dichlorides



compound[a]	θ (deg)	α (deg)
$Cp^*_2HfH_2$	144.1(2)	145.2(2)
	145.0(2)	145.9(2)
$Cp^*\{\eta^5\text{-}C_5H_4(CMe_3)\}ZrCl_2$ (**1**)	130.68(1)	124.73(1)
$Cp^*\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}ZrCl_2$ (**3**)	131.49(2)	126.87(8)
$\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrCl_2$ (**6**)	129.7(1)	121.1(1)
Cp_2HfCl_2 (ref 30)	129.23	126.54
	129.14	127.60
$Cp^*CpHfCl_2$ (ref 31)	130.59	126.70
$(C_5H_4\text{-}CH_2CH_3)_2HfCl_2$ (ref 32)	129.96	125.71

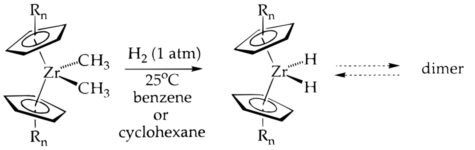
[a] A search of the Cambridge Structural Database produced 3 hafnocene dichloride complexes. Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Smith, J. M.; Watson, D. G. *J. Chem. Info. Comp. Sci.* **1991**, *31*, 187.

Treatment of the metallocene dichloride complexes with 2 equiv of methyllithium in diethyl ether affords the zirconocene dimethyl complexes in good yields (eq 1). The dimethyl complexes are air-sensitive and are readily soluble in aromatic, hydrocarbon, and ethereal solvents. For each compound, a diagnostic Zr−C*H_3* resonance in the ^1H NMR spectrum is observed slightly upfield of $SiMe_4$ (see Experimental Section). Purification of these compounds can be achieved either by recrystallization from cold petroleum ether or by sublimation at 80 °C (10^{-4} Torr).



(1)

Hydrogenation of the entire series of dimethylzirconcenes proceeds readily and quantitatively (^1H NMR), even at room temperature and 1 atm H_2, unlike the more forcing conditions previously reported for the preparation of zirconocene dihydrides from the dimethyl derivatives (eq 2). The resulting highly air-sensitive dihydride complexes are soluble in aromatic solvents. In general, the dimeric dihydrides are less soluble than the monomeric dihydrides. This procedure provides an attractive alternate route to previously reported $[Cp^*CpZrH_2]_2$ (Cp = (η^5-C_5H_5)).[13]



(2)

Hydrogenation of $Cp^*(Ind)ZrMe_2$ results in quantitative formation of $[Cp^*(THI)ZrH_2]_2$ (**11**), as a result of σ bond metathesis reactions of the Zr-CH_3 with H_2 and subsequent hydrogenation of the indenyl ring. This finding is similar to that reported for the hydrogenation of bis(indenyl)zirconium dimethyl.[5] Monitoring the reaction of $Cp^*(Ind)ZrMe_2$ with H_2 by ^1H NMR reveals the intermediacy of $Cp^*(THI)ZrMe_2$, suggesting that the zirconocene dihydride that is generated in the early stages of the reaction serves as a catalyst for hydrogenation of the benzo groups of both starting $Cp^*(Ind)ZrMe_2$ and initially formed $Cp^*(Ind)ZrH_2$. This suggestion is further supported by the qualitative rate enhancement for final conversion to **11** that is observed

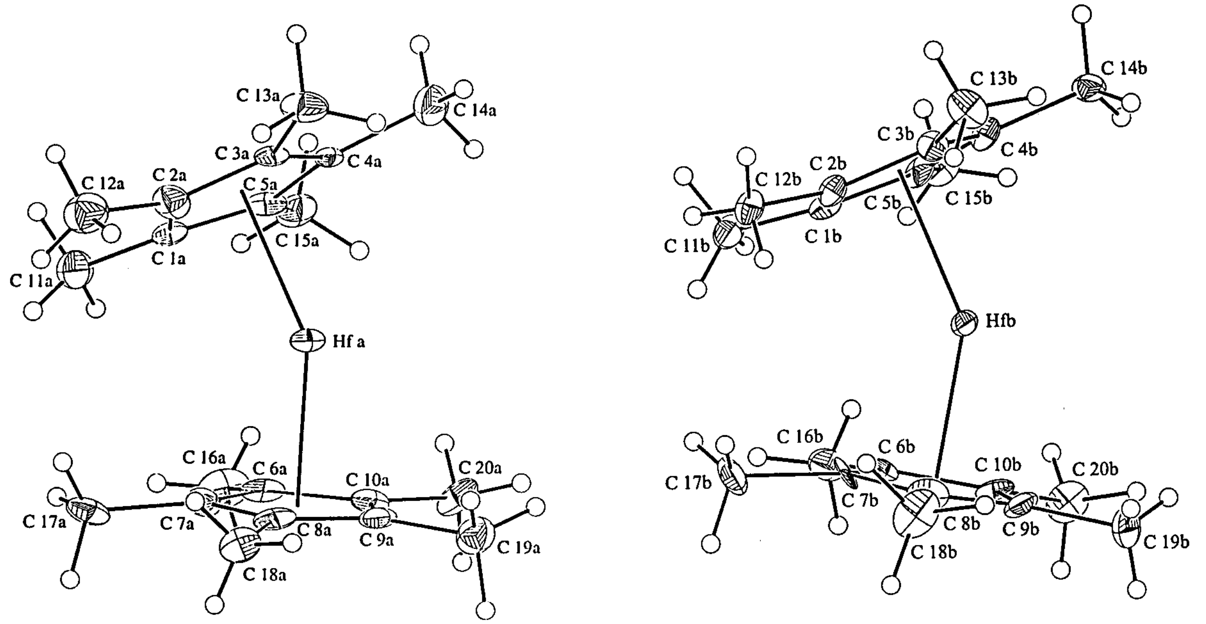


Figure 4. Molecular structure of (η^5-C_5Me_5)$_2$HfH_2 (50% probability ellipsoids).

Table 2. Molecular Weights for Zirconocene Dihydrides and Molecularity Indicated by ^{1}H NMR Spectroscopy

compound	MW[a]	[Zr] (M)	molecularity in soln[b]
[Cp*CpZrH_2]$_2$	606 (294)	ref 13	dimeric
[Cp*(η^5-C_5H_4-CMe$_3$)ZrH_2]$_2$ (**8**)	675 (348)	0.013	dimeric
[Cp*(THI)ZrH_2]$_2$ (**11**)	670 (344)	0.040	dimeric
[{η^5-C_5H_3-1,3-(CHMe$_2$)$_2$}$_2$ZrH_2]$_2$ (**14**)	773 (392)	0.014	dimeric
[Cp*{η^5-C_5H_3-1,3-(CHMe$_2$)$_2$}ZrH_2]$_2$ (**10**)	740 (369)	0.049	monomer and dimer obsd
[(η^5-C_5HMe$_4$)$_2$ZrH_2]$_2$ (**15**)	564 (335)	0.041	monomer and dimer obsd
Cp*{η^5-C_5H_3-1,3-(CMe$_3$)$_2$}ZrH_2 (**9**)	446 (406)	0.044	monomeric
Cp*(η^5-C_5H_2-1,2,4-Me$_3$)ZrH_2	342 (336)	ref 13	monomeric
{η^5-C_5H_3-1,3-(CMe$_3$)$_2$}$_2$ZrH_2 (**13**)	480 (448)	0.033	monomeric
Cp*(η^5-C_5HMe$_4$)ZrH_2 (**12**)	346 (349)	0.029	monomeric
Cp*$_2$ZrH_2	402 (394)	ref 12a	monomeric

[a] Solution molecular weights determined by ebulliometry at indicated concentration in benzene-d_6 (calculated MW for monomer). Errors in molecular weights are estimated as ±20%. [b] Molecularity at 296 K as established by ^{1}H NMR in benzene-d_6 or toluene-d_8 (see text).

when Cp*(Ind)ZrMe$_2$ is hydrogenated in the presence of **11**. Moreover, **11** also catalyzes the hydrogenation of dibenzoferrocene[15] to bis(tetrahydroindenyl)iron.[16]

Proton NMR spectroscopy has proven particularly useful for the characterization of the new zirconocene dihydride complexes.[5] The number of zirconium hydride resonances observed and their chemical shifts are useful in determining the molecularity of the dihydride species in solution. Monomeric zirconium dihydrides exhibit a single downfield resonance ($\delta \approx 7$ to 8), whereas dimeric dihydrides display separate resonances for terminal ($\delta \approx 4$ to 5) and bridging hydrides ($\delta \approx 1$ to -1). Solution molecular weights for the new dihydrides and ^{1}H NMR determined molecularities, along with those for previously reported Cp*$_2$ZrH_2,[12a] [Cp*(η^5-C_5H_5)ZrH_2]$_2$,[13] and [Cp*(η^5-C_5H_2-1,2,4-Me$_3$)ZrH_2]$_2$[13] are given in Table 2.

In all cases, the measured molecular weights and ^{1}H NMR data are in agreement. Thus, for example, the molecular weight indicates that Cp*$_2$ZrH_2 is monomeric, and accordingly a single resonance at δ 7.46 is observed at room temperature in benzene-d_6 for the equivalent ZrH_2. Similarly, monomeric Cp*(η^5-C_5HMe$_4$)ZrH_2 (**12**), Cp*{η^5-C_5H_3-1,3-(CMe$_3$)$_2$}ZrH_2 (**9**), and {η^5-C_5H_3-1,3-(CMe$_3$)$_2$}$_2$ZrH_2 (**13**) exhibit singlets at δ 7.45, δ 7.09, and δ 7.36, respectively, for their Zr*H*$_2$.

The other dihydride complexes exhibit ^{1}H NMR spectra that are quite temperature-dependent, suggesting equilibria between at least two forms. Thus, the 500 MHz spectrum for [Cp*CpZrH_2]$_2$ at room temperature displays no resonances attributable to Zr*H*$_2$. Cooling a sample to 250 K in toluene-d_8 solution allows for observation of signals for terminal (δ 4.26 br, multiplet) and bridging (δ -2.65 br, multiplet) hydrides and one set of cyclopentadienyl resonances (δ 5.72 (η^5-C_5H_5) and δ 1.93 {η^5-C_5(CH_3)$_5$}. Somewhat unexpectedly, further cooling to 225 K reveals two sets of hydride signals (δ 4.31 multiplet and δ 4.14 multiplet; δ -0.10 quartet, $J_{H-H} = 15$ Hz and δ -2.68 br, multiplet) and two sets of cyclopentadienyl resonances (δ 5.77 (major) and δ 5.65 (minor); δ 2.00 (minor) and δ 1.95 (major); [major]:[minor] ≈ 3:1). These data suggest that above 225 K *two* dimeric hydride isomers are in rapid equilibrium, presumably the cis and trans isomers via monomeric [Cp*CpZrH_2] as shown in Scheme 2. Considering the unfavorable steric interactions between cyclopentadienyl ligands across the [HZr(μ_2-H)$_2$ZrH] units, we tentatively assign the major isomer as trans (Scheme 2).

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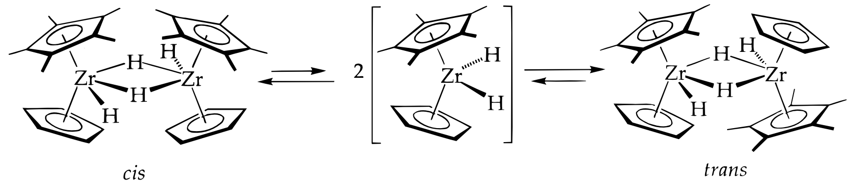
(15) Wilkinson, G.; Pauson, P. L. *J. Am. Chem. Soc.* **1954**, *70*, 2024.

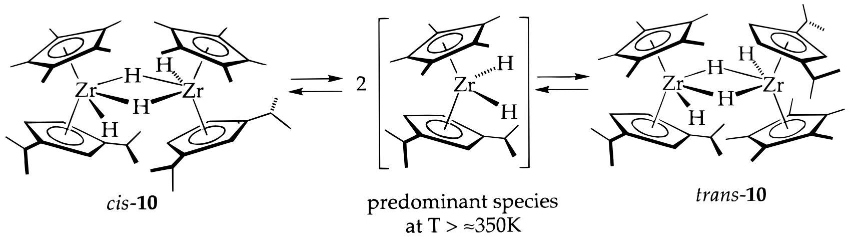
(16) Hydrogenation of *rac*-(EBI)ZrMe$_2$ in benzene solution affords the previously reported {*rac*-(EBTHI)ZrH_2}$_2$ in 57% yield. See ref 8.

(17) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

Scheme 2



Scheme 3

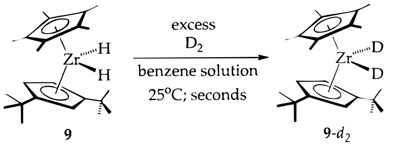


The related complex $[Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrH_2]_2$ (**8**) exhibits very similar behavior, although the two isomeric dihydride dimers are observable at room temperature in approximately equal amounts. Signals for the terminal hydrides are observed at δ 4.08 (br, multiplet) and δ 3.90 (br, multiplet), whereas the bridging hydrides appear at δ −0.76 and δ −2.56. Heating the sample in cyclohexane-d_{12} to 340 K results in coalescence of the peaks attributable to protons of the Cp* (δ 1.97) and CMe_3 (δ 1.38) groups. Curiously, the more sterically congested (**8**) undergoes slower isomer interconversion in comparison to $[Cp^*CpZrH_2]_2$.

Variable temperature NMR studies on $[Cp^*(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}CHMe_2)ZrH_2]_2$ (**10**) reveal yet another dynamic equilibrium for this complex. At room temperature, the 500 MHz NMR spectrum displays a single set of ligand resonances in addition to a broad signal centered at δ 4.06 for the zirconium hydride resonance, intermediate between those found for the monomeric and dimeric chemical shift values. We interpret a shift in this range as a weighted average between monomeric and dimeric dihydrides that are in rapid equilibrium. Cooling a sample of **10** [Zr] = 0.049 M) to 200 K in toluene-d_8 allows for observation of roughly equal amounts of two isomeric dihydride dimers. Terminal hydride resonances are observed at δ 4.20 and δ 3.92, whereas bridging hydrides appear at δ −1.14 and δ −1.25. Warming the sample to 240 K results in coalescence of the $CHMe_2$ peaks (δ 1.39), as well as the terminal hydrides (δ 4.02). At 250 K, the signals attributable to the protons of the Cp* ligands for the two isomers coalesce at δ 2.05. Continued heating of a sample of **10** above room temperature results in a gradual shift of the zirconium hydride resonance downfield, implicating increased concentration of the monomeric dihydride at higher temperatures. At 310 K, the zirconium hydride appears as a broad singlet centered at δ 5.45, and at 340 K the resonance shifts to δ 6.70. At 360 K, the hydride resonance approaches its maximum value of δ 6.90, and the value of the chemical shift of this peak does not change with further heating of the sample (T = 380 K). At these temperatures, we propose that monomeric **10** is the predominant species in solution (Scheme 3).

Variable temperature NMR data for $(\eta^5\text{-}C_5Me_4H)_2ZrH_2$ (**15**) also reveal significant amounts of both monomer and dimer in rapid equilibrium. Thus, the 500 MHz NMR spectrum at 296 K ([Zr] = 0.041 M) displays a very broad singlet for the zirconium hydride resonance centered at δ 2.80. Warming of the sample results in both a sharpening of the zirconium hydride resonance and a shift downfield. As with **10**, the spectrum of **15** at 380 K in benzene-d_6 solution displays a zirconium hydride resonance at δ 7.11, implicating the presence of a monomeric zirconocene hydride. At temperatures between 296 and 380 K, the chemical shift gradually shifts downfield from δ 2.80 to δ 7.11. Perhaps the most intriguing feature of **15** is its ability to form hydride bridges and hence a dimer, albeit only at low temperatures. Considering that $Cp^*_2ZrH_2$ and **12** are monomeric, it is quite remarkable that removal of one methyl group from the other $(\eta^5\text{-}C_5Me_5)$ ligand of **12** is sufficient to permit formation of a dimeric **15**. Clearly, there is just enough steric protection to dimer formation for both $Cp^*_2ZrH_2$ and **12**.

H/D Exchange Reactions for Zirconocene Dihydrides with D_2. When each member of the series of zirconocene dihydrides is exposed to 1 atm of dideuterium in benzene solution, rapid exchange of hydride ligands is observed (e.g., eq 3). The rate of exchange is

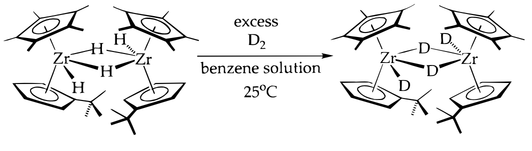


9 9-d_2

(3)

sufficiently rapid to be observed by ^1H NMR. Exposure of a benzene-d_6 solution of **9** to 1 atm of H_2 results in broadening and upfield shifting of the ZrH_2 resonance (toward that for dissolved H_2); no resonance for H_2 is observed, indicative of exchange on the ^1H NMR time scale.

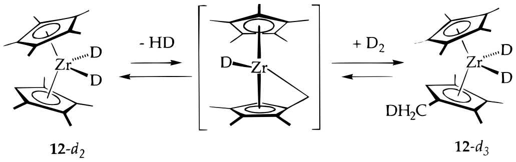
Treatment of dimeric **8** and **11** with dideuterium results in rapid exchange of deuterium into both bridging and terminal hydride positions at room temperature (e.g., eq 4). Although we are unable to rule out direct



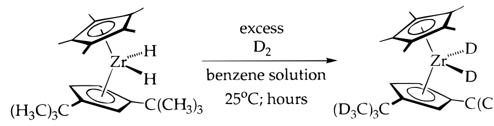
(4)

reaction of D_2 with the terminal and/or bridging hydride ligands of the dimers, rapid exchange of both bridging and terminal hydride positions of the dimeric complexes suggests a facile monomer−dimer equilibrium (consistent with the variable temperature ^1H NMR studies above), allowing for rapid incorporation of deuterium into both hydride positions.

Deuterium incorporation into the C−H positions of the cyclopentadienyl ligands is much slower than for the hydride positions, and H/D exchange occurs preferentially only with certain of the C−H bonds of the monomeric dihydride complexes. Thus, reaction of monomeric $Cp^*_2ZrH_2$ with D_2 at 23 °C results in gradual incorporation of deuterium into the C−H positions of the two (η^5-C_5Me_5) ligands over a period of 12 h. Benzene-d_6 solutions of Cp*(η^5-C_5HMe_4)ZrH_2 (**12**) under D_2 result in rapid exchange of the two hydride positions at room temperature, and over the course of several hours at 25 °C, selective deuteration of the Cp* ligands and two of the methyl groups (those that appear at δ 1.81 in the ^1H NMR spectrum) of the tetramethylcyclopentadienyl ligand occurs; the latter is approximately five times faster than the former. NOE difference spectroscopy reveals that these are the 1,4 methyl groups of the (η^5-C_5Me_4H) ligand. Thus, irradiation of the methyl groups at δ 1.81 results in an NOE enhancement of the (η^5-C_5Me_4H) resonance, whereas irradiation of the downfield methyl groups (δ 2.45) does not produce a detectable NOE enhancement. Deuteration of the two other methyl groups of the (η^5-C_5Me_4H) ligand is eventually observed (^2H NMR), although this exchange occurs at a much slower rate, requiring several days at room temperature or several hours at 80 °C. Similar observations have been made by Parkin et al. that exposure of [{$Me_2Si(\eta^5$-$C_5Me_4)_2$}ZrH_2]$_2$ to D_2 results in rapid exchange of the hydride positions and slower deuterium incorporation preferentially into the methyl groups α to the [$SiMe_2$] linker.[18] As might be expected, the X-ray structure of (η^5-C_5HMe_4)$_2ZrCl_2$ reveals that the less hindered C−H groups are in the narrow back portion of the zirconocene wedge.[19] Taken together, these observations suggest that the methyl groups that are most accessible for formation of "tuck-in" intermediates are those directed toward the side of the metallocene wedge in the ligand array (eq 5). The remarkably exacting orientations for metalation of a methyl-substituted cyclopentadienyl ligand is perhaps most evident in the H/D exchange reactions for Cp*{η^5-C_5H_3-1,3-$(CMe_3)_2$}ZrH_2 (**9**). Treatment of **9** with D_2 at 23 °C results in slow exchange with the C−H positions of the CMe_3 groups over a period of several hours. Interestingly, no deuterium incorporation into the Cp* ligand (or remaining three C−H bonds of the {η^5-C_5H_3-1,3-$(CMe_3)_2$} ligand) is observed under these conditions (eq 6). Because no tuck-in derivative resulting from metalation of a CMe_3 group builds up to ^1H NMR detectable concentrations under these conditions, we conclude that the two *tert*-butyl substituents of the other cyclopentadienyl ligand must constrain the Cp* ligand in orientations unsuited to metalation of a methyl group.



12-d_2 **12**-d_3 (5)



9 **9**-d_{20} (6)

Treatment of dimeric [Cp*{η^5-C_5H_3-1,3-$(CHMe_2)_2$}-ZrH_2]$_2$ (**10**) or [(η^5-C_5HMe_4)$_2ZrH_2$]$_2$ (**15**) with dideuterium in benzene-d_6 rapidly leads to exchange of the hydride positions but not the methyl groups of the Cp*, isopropyl substituents, or η^5-C_5HMe_4 ligands, even after several days at room temperature.[20] This large reduction in rate likely reflects the requirement that formation of the tuck-in intermediates occurs from the monomer, which is present in only very low concentrations for the (predominantly) dimeric complexes.

Conclusions

A series of zirconocene dihydride complexes of the general form, [$(R_nCp)_2ZrH_2$]$_x$, having substituted cyclopentadienyl ligands, has been prepared by hydrogenation of the corresponding dimethyl complexes. The molecularity of these compounds in solution varies with the size and/or number of alkyl substituents on the cyclopentadienyl rings. The most sterically crowded members of the series, Cp*{η^5-C_5H_3-1,3-$(CMe_3)_2$}ZrH_2 (**9**), Cp*(η^5-C_5HMe_4)ZrH_2 (**12**), and {η^5-C_5H_3-1,3-$(CMe_3)_2$}$_2ZrH_2$ (**13**), are monomeric; the less crowded members, [Cp*(η^5-C_5H_4-CMe_3)ZrH_2]$_2$ (**8**), [Cp*(THI)-ZrH_2]$_2$ (**11**), and [{η^5-C_5H_3-1,3-$(CHMe_2)_2$}$_2ZrH_2$]$_2$ (**14**), are predominantly dimeric in solution, whereas [Cp*-{η^5-C_5H_3-1,3-$(CHMe_2)_2$}ZrH_2]$_2$ (**10**) and [(η^5-C_5HMe_4)$_2$-ZrH_2]$_2$ (**15**) form equilibrium mixtures of both monomers and dimers, the predominant form depending on temperature and concentration. Variable temperature NMR studies on the dimeric dihydride complexes having mixed cyclopentadienyl ligands, e.g., **9** and even [Cp*Cp-ZrH_2]$_2$, reveal comparable amounts of two different dimeric hydrides, presumably cis and trans isomers. It is likely that unfavorable steric interactions in the cis isomers are relieved by twisting of the two zirconocene units such that their "equatorial planes" are not coincident. Such twisting has been established for an *ansa*-titanocene monohydride[21] and for *ansa*-yttrocene hydrides.[22]

Whether monomeric or dimeric, the hydride ligands of these dihydride complexes undergo rapid exchange with D_2. For the monomeric members of the series, further H/D exchange leads to incorporation of deuterium into some of the alkyl substituents of the cyclo-

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(20) Under more forcing conditions (ca. 2 atm D_2, 80 °C, 12 h, benzene−d_6) H/D exchange for the methyl groups of the (η^5-C_5HMe_4) ligands is accompanied by formation of (η^5-C_5HMe_4)$_2$Zr(H)($C_6D_xH_{5-x}$) and cyclohexane−d_n. Chirik, P. J.; Bercaw J. E., to be published.

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pentadienyl ligands. The likely mechanism involves the monomeric dihydride undergoing intramolecular σ bond metathesis between an alkyl C−H bond and a Zr−H bond, leading to tuck-in intermediates. The relative rates for H/D exchange of methyl substituents indicate this process has a strong orientational preference for the back of the zirconcene wedge. *tert*-Butyl groups undergo H/D exchange at a similar rate. Metalation of these C−H bonds also likely involves a reversible, intramolecular σ bond metathesis process analogous to that reported earlier for $(\eta^5\text{-}C_5Me_4R)_2ZrH_2$ (R = CH_3, CH_2CH_3, CH_2CMe_3).[17]

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques, or in a drybox under a nitrogen atmosphere as described previously.[23] Molecular weights were determined by ebulliometry as described previously.[23] Argon, dinitrogen, dihydrogen, and dideuterium were purified by passage over columns of MnO on vermiculite and activated molecular sieves. Solvents for air- and moisture-sensitive reactions were stored under vacuum over titanocene[24] or sodium−benzophenone ketyl. Toluene-d_8 and cyclohexane-d_{12} were distilled from sodium−benzophenone ketyl and stored over titanocene. Preparations of $C_5H_5\text{-}CMe_3$,[25] $C_5H_3\text{-}1,3\text{-}CMe_3$,[26] $C_5H_3\text{-}1,3\text{-}CHMe_2$,[27] Cp^*ZrCl_3,[13] $(\eta^5\text{-}C_5HMe_4)_2ZrCl_2$,[19] and lithium indenide[28] were carried out as described previously. Tetramethylcyclopentadiene was purchased from Quantum Chemical Company and used as received. Preparation of the lithiocyclopentadienides was accomplished via addition of 1.6 M *n*-BuLi to a petroleum ether solution of the cyclopentadiene followed by filtration.

NMR spectra were recorded on a Bruker AM500 (500.13 MHz for ^1H, 125.77 MHz for ^{13}C) spectrometer. All ^1H and ^{13}C NMR chemical shifts are relative to TMS using ^1H (residual) or ^{13}C chemical shifts of the solvent as a secondary standard. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey. Complete combustion of the zirconocene dihydrides has proven difficult, and many times V_2O_5 or Thermolite oxidant was added in order to gain satisfactory analyses.

$Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrCl_2$ (1). A 250 mL round-bottom flask equipped with stir bar was charged with Cp^*ZrCl_3 (5.16 g, 15.60 mmol) and Me_3CCpLi (2.00 g, 15.60 mmol), and a 180° needle valve was attached. On the vacuum line, 100 mL of toluene was added by vacuum transfer, and the reaction mixture was warmed to room temperature and stirred for 5 days. Toluene was removed in vacuo, leaving a yellow solid. In air, about 50 mL of CH_2Cl_2 was added along with 20 mL of 4 M HCl. The CH_2Cl_2 layer was separated and combined with the 15 mL extracts of the aqueous layer. The CH_2Cl_2 solution was dried over $MgSO_4$ and filtered. Crystallization from CH_2Cl_2/hexanes afforded (**1**) in 60.5% yield (3.94 g). Anal. Calcd for $C_{19}H_{28}Zr_1Cl_2$: C, 54.52; H, 6.74. Found: C, 54.63; H, 6.82. ^1H NMR (benzene-d_6): $\delta = 1.80$ (s, 15H, Cp*), 1.45 (s, 9H, $C\mathit{Me}_3$), 6.15 (m, 2H, $C_5\mathit{H}_4$); 5.55 (m, 2H, $C_5\mathit{H}_4$). ^{13}C NMR (benzene-d_6): $\delta = 12.60$ ($C_5\mathit{Me}_5$), 112.6 (C_5Me_5); 32.45 ($C\mathit{Me}_3$), 146.6 ($\mathit{C}Me_3$); 118.4, 122.5 ($\mathit{C}_5H_4CMe_3$).

$Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrMe_2$. A medium frit assembly was charged with $Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrCl_2$ (2.20 g, 5.28 mmol) and evacuated. Et_2O was added by vacuum transfer at −78 °C forming a slurry. At −78 °C, against an Ar counterflow, 1.4 M MeLi (8.30 mL, 11.60 mmol) solution was added via syringe. The reaction mixture was stirred and warmed to room temperature. With stirring, a clear solution and white precipitate formed. The reaction mixture was stirred for 16 h, after which time the Et_2O was removed in vacuo and replaced with toluene. The yellow toluene solution was filtered, and the remaining white precipitate was washed with toluene. The toluene was removed, leaving a yellow powder. Recrystallization from cold petroleum ether affords $Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrMe_2$ in 60.4% yield (1.20 g). Anal. Calcd for $C_{21}H_{34}Zr_1$: C, 66.78; H, 9.07. Found: C, 65.96; H, 9.11. ^1H NMR (benzene-d_6): $\delta = 1.74$ (s, 15H, Cp*), 1.26 (s, 9H, $C\mathit{Me}_3$), −0.30 (s, 6H, $Zr\text{-}C\mathit{H}_3$), 5.80 (m, 2H, $C_5\mathit{H}_4$); 5.44 (m, 2H, $C_5\mathit{H}_4$). ^{13}C NMR (benzene-d_6): $\delta = 12.11$ ($C_5\mathit{Me}_5$), 110.15 (C_5Me_5); 32.25 ($C\mathit{Me}_3$), 142.97 ($\mathit{C}Me_3$), 33.17 ($Zr\text{-}\mathit{C}H_3$) 117.82, 108.67 ($\mathit{C}_5H_4CMe_3$).

$[Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrH_2]_2$ (8). In the drybox, a thick-walled glass reaction vessel equipped with stir bar was charged with $Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrMe_2$ (0.754 g, 2.01 mmol). On the vacuum line, the thick-walled reaction vessel was evacuated, and about 25 mL of petroleum ether was added by vacuum transfer. The reaction vessel was warmed to room temperature and 1 atm of H_2 was admitted. The reaction vessel was sealed, and the mixture was stirred for 1 week, depositing a white solid over time. The reaction vessel was taken into the drybox, the contents was transferred into a frit assembly, and the solid was collected on the frit and washed with cold petroleum ether. Drying the solid in vacuo for 5 h affords $[Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrH_2]_2$ in 65% yield (0.452 g). Anal. Calcd for $C_{19}H_{30}Zr$: C, 65.26; H, 8.65. Found (V_2O_5 oxidant): C, 63.37; H, 8.61. Found (added Thermolite oxidant): C, 60.50; H, 8.34. ^1H NMR (benzene-d_6): $\delta = 1.95$, 1.97 (s, 15H, Cp*), 1.36, 1.39 (s, 9H, $C\mathit{Me}_3$), 4.08, 3.09 (m, 2H, $Zr\text{-}\mathit{H}_t$), −0.76, −2.56 (m, 2H, $Zr\text{-}\mathit{H}_b$), 4.55, 4.83, 4.96, 5.85, 6.07, 6.62 (m, $C_5\mathit{H}_4$). ^{13}C NMR (benzene-d_6): $\delta = 13.77$, 13.89 ($C_5\mathit{Me}_5$), 115.85, 116.01 (C_5Me_5); 33.26, 33.36 ($C\mathit{Me}_3$), 141.40, 141.62 ($\mathit{C}Me_3$); 105.50, 104.85, 104.50, 103.49, 103.07, 100.70, 98.65 ($\mathit{C}_5H_4CMe_3$).

$Cp^*(Indenyl)ZrCl_2$ (4). This compound was prepared in the same manner as **1** with 4.10 g (12.34 mmol) of Cp^*ZrCl_3 and 1.52 g of lithium indenide (12.34 mmol). Crystallization from CH_2Cl_2/hexanes afforded $Cp^*(Indenyl)ZrCl_2$ in 82.4% yield (4.20 g). Anal. Calcd for $C_{19}H_{22}Zr_1Cl_2$: C, 55.32; H, 5.38. Found: C, 55.22; H, 5.10. ^1H NMR (benzene-d_6): $\delta = 1.81$ (s, 15H, Cp*), 5.89 (m, 2H, Cp); 5.80 (m, 2H, Cp), 7.08 (m, 2H, benzo), 7.51 (m, 2H, benzo). ^{13}C NMR (benzene-d_6): $\delta = 12.69$ ($C_5\mathit{Me}_5$), 104.27 (C_5Me_5), 118.30, 121.87, 123.50, 125.72, 127.04 (Ind).

$Cp^*(Indenyl)ZrMe_2$. This compound was prepared in the same manner as $Cp^*(\eta^5\text{-}C_5H_4\text{-}CMe_3)ZrMe_2$ with 2.35 g of $Cp^*(Indenyl)ZrCl_2$ (5.69 mmol) and 8.90 mL of 1.4 M MeLi. Recrystallization from cold petroleum ether affords $Cp^*(Indenyl)ZrMe_2$ in 70.8% yield (1.50 g). Anal. Calcd for $C_{21}H_{28}Zr_1$: C, 67.86; H, 7.56. Found: C, 67.88; H, 8.06. ^1H NMR (benzene-d_6): $\delta = 1.71$ (s, 15H, Cp*), −0.84 (s, 3H, $Zr{-}C\mathit{H}_3$), 5.81 (m, 2H, Cp); 5.37 (m, 2H, Cp), 7.39 (m, 2H, benzo), 7.09 (m, 2H, benzo). ^{13}C NMR (benzene-d_6): $\delta = 11.79$ ($C_5\mathit{Me}_5$), 100.70 (C_5Me_5), 36.06 ($Zr\text{-}\mathit{C}H_3$), 117.45, 118.34, 122.78, 124.61, one peak not located (Ind).

$[Cp^*(THI)ZrH_2]_2$ (11). This compound was prepared in the same manner as **8** with 1.35 g of $Cp^*(Indenyl)ZrMe_2$ (3.63 mmol) yielding $[Cp^*(THI)ZrH_2]_2$ in 68.0% yield (0.850 g). Anal. Calcd for $C_{19}H_{28}Zr_1$: C, 65.64; H, 8.12. Found (with V_2O_5 oxidant): C, 65.46; H, 8.36. ^1H NMR (benzene-d_6): $\delta = 2.01$ (s, 15H, Cp*), 5.18 (s, 2H, $Zr\text{-}\mathit{H}_t$), −1.86 (s, 2H, $Zr\text{-}\mathit{H}_b$), 5.78 (m, 1H, Cp); 5.01 (m, 1H, Cp), 4.65 (m, 1H, Cp), 0.85, 1.92, 2.12, 2.65 (m, THI). ^{13}C NMR (benzene-d_6): $\delta = 13.61$ ($C_5\mathit{Me}_5$),

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116.47 (*C*$_5$Me$_5$), 98.78, 103.45, 108.93 (Cp), 22.38, 24.36, 25.17, 28.03 (THI).

Cp*{η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$}ZrCl$_2$ (3). This compound was prepared in the same manner as **1** with 2.73 g of Cp*ZrCl$_3$ (8.22 mmol) and 1.22 g of {C$_5$H$_3$-1,3-(CHMe$_2$)$_2$}Li (8.22 mmol). Crystallization from CH$_2$Cl$_2$/hexanes afforded Cp*(η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$)ZrCl$_2$ in 83.3% yield (3.00 g). Anal. Calcd for C$_{21}$H$_{32}$Zr$_1$Cl$_2$: C, 56.48; H, 7.22. Found: C, 56.53; H, 7.32. ^{1}H NMR (benzene-*d*$_6$): $\delta = 1.83$ (s, 15H, Cp*), 3.19 (sept, 2H, C*H*Me$_2$), 0.96 (d, 6H, CH*Me*$_2$), 1.16 (d, 6H, CH*Me*$_2$), 5.30 (d, 2H,C$_5$*H*$_3$) 6.05 (t, 1H, C$_5$*H*$_3$). ^{13}C NMR (benzene-*d*$_6$): 11.34 (C$_5$*Me*$_5$), 106.47 (*C*$_5$Me$_5$); 36.06 (*C*HMe$_2$), 22.00, 23.85 (CH*Me*$_2$), 112.5, 114.73, 122.84 (*C*$_5$H$_3$).

Cp*{η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$}ZrMe$_2$. This compound was prepared in the same manner as Cp*(η^5-C$_5$H$_4$-CMe$_3$)ZrMe$_2$ with 2.00 g of Cp*{η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$}ZrCl$_2$ (4.56 mmol) and 6.80 mL of 1.4 M MeLi (9.56 mmol). Recrystallization from cold petroleum ether affords Cp*{η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$}ZrMe$_2$ in 91.2% yield (1.65 g). Anal. Calcd for C$_{23}$H$_{38}$Zr$_1$: C, 68.08; H, 9.44. Found: C, 68.06; H, 9.22. ^{1}H NMR (benzene-*d*$_6$): $\delta =$ 1.78 (s, 15H, Cp*), -0.39 (s, 3H, Zr-C*H*$_3$), 2.83 (sept, 2H, C*H*Me$_2$), 0.94 (d, 6H, CH*Me*$_2$), 1.22 (d, 6H, CH*Me*$_2$), 4.93 (d, 2H,C$_5$*H*$_3$) 6.05 (t, 1H, C$_5$*H*$_3$). ^{13}C NMR (benzene-*d*$_6$): 12.08 (C$_5$*Me*$_5$), 103.30 (*C*$_5$Me$_5$); 28.84 (Zr-*C*H$_3$), 35.79 (*C*HMe$_2$), 22.70, 25.90 (CH*Me*$_2$), 111.42, 117.68, 137.78 (*C*$_5$H$_3$).

[Cp*(η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$)ZrH$_2$]$_2$ (10). This compound was prepared in the same manner as **8** with 0.680 g of Cp*{η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$}ZrMe$_2$ (1.71 mmol). Recrystallization from cold petroleum ether affords [Cp*({η^5-C$_5$H$_3$-1,3-(CHMe$_2$)$_2$}ZrH$_2$]$_2$ in 72.2% yield (0.456 g). Anal. Calcd for C$_{21}$H$_{34}$Zr$_1$: C, 66.78; H, 9.07. Found: C, 67.13; H, 9.04. ^{1}H NMR (benzene-*d*$_6$): $\delta = 2.05$ (s, 15H, Cp*), 4.06 (br s, 2H, Zr-*H*$_2$), 3.21 (sept, 2H, C*H*Me$_2$), 1.27 (d, 6H, CH*Me*$_2$), 1.30 (d, 6H, CH*Me*$_2$), 5.03 (d, 2H,C$_5$*H*$_3$) 6.15 (t, 1H, C$_5$*H*$_3$). ^{13}C NMR (benzene-*d*$_6$): 13.44 (C$_5$*Me*$_5$), 107.55 (*C*$_5$Me$_5$), 30.01 (*C*HMe$_2$), 25.58, 23.77 (CH*Me*$_2$), 95.51, 103.16, 118.48(*C*$_5$H$_3$).

Cp*{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}ZrCl$_2$ (2). This compound was prepared in the same manner as **1** with 3.00 g of Cp*ZrCl$_3$ (10.09 mmol) and 3.62 g of {C$_5$H$_3$-1,3-(CMe$_3$)$_2$}Li(DME)$_{1.5}$ (10.09 mmol). Recrystallization from CH$_2$Cl$_2$/hexanes afforded Cp*{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}ZrCl$_2$ in 71.0% yield (3.56 g). Anal. Calcd for C$_{23}$H$_{36}$Zr$_1$Cl$_2$: C, 58.20; H, 7.62. Found: C, 57.75; H, 7.89. ^{1}H NMR (benzene-*d*$_6$): $\delta = 1.82$ (s, 15H, Cp*), 1.28 (s, 18H, C*Me*$_3$), 5.46 (d, 2H, C$_5$*H*$_3$), 6.38 (d, 1H, C$_5$H$_3$). ^{13}C NMR (benzene-*d*$_6$): 12.05 (C$_5$*Me*$_5$), 113.45 (*C*$_5$Me$_5$), 31.60 (C*Me*$_3$), 142.50 (*C*Me$_3$), 109.75, 114.63, 123.50 (*C*$_5$H$_3$).

Cp*{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}ZrMe$_2$. This compound was prepared in the same manner as Cp*{η^5-C$_5$H$_4$-CMe$_3$]ZrMe$_2$ with 1.25 g of Cp*{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}ZrCl$_2$ (2.64 mmol) and 4.10 mL of 1.4 M MeLi (5.79 mmol). Recrystallization from cold petroleum ether affords Cp*{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}ZrMe$_2$ in 84.1% yield (0.96 g). Anal. Calcd for C$_{23}$H$_{36}$Zr$_1$: C, 68.42; H, 8.99. Found: C, 68.26; H, 9.30. ^{1}H NMR (benzene-*d*$_6$): $\delta =$ 1.78 (s, 15H, Cp*), -0.20 (s, 6H, Zr-C*H*$_3$), 1.25 (s, 18H, C*Me*$_3$), 5.00 (d, 2H, C$_5$*H*$_3$), 6.41 (d, 1H, C$_5$H$_3$). ^{13}C NMR (benzene-*d*$_6$): 12.28 (C$_5$*Me*$_5$), 117.86 (*C*$_5$Me$_5$), 33.95 (Zr-*Me*), 31.93 (C*Me*$_3$), 143.18 (*C*Me$_3$), 103.82, 106.87, 130.54 (*C*$_5$H$_3$).

Cp*{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}ZrH$_2$ (13). This compound was prepared in the same manner as **8** with 0.950 g of Cp*(η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$)ZrMe$_2$ (2.19 mmol). Drying the solid in vacuo for several hours affords Cp*{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}ZrH$_2$ in 78.8% yield (0.700 g). Anal.Calcd for C$_{21}$H$_{32}$Zr: C, 60.08; H, 9.44. Found: C, 66.60; H, 8.60. Found (added Thermolite oxidant): C, 66.85; H, 9.14. ^{1}H NMR (benzene-*d*$_6$): $\delta = 2.05$ (s, 15H, Cp*), 7.09 (s, 2H, Zr-*H*$_2$), 1.30 (s, 18H, C*Me*$_3$), 4.92 (d, 2H, C$_5$*H*$_3$), 6.70 (d, 1H, C$_5$H$_3$). ^{13}C NMR (benzene-*d*$_6$): 13.06 (C$_5$*Me*$_5$), 101.08 (*C*$_5$Me$_5$), 32.22 (C*Me*$_3$), 135.45 (*C*Me$_3$), 105.60, 109.08, 120.04 (*C*$_5$H$_3$).

Cp*(η^5-C$_5$HMe$_4$)ZrCl$_2$ (5). A 100 mL round-bottom flask equipped with stir bar was charged with Cp*ZrCl$_3$ (3.00 g, 9.03 mmol) and (C$_5$HMe$_4$)Li (1.15 g, 9.03 mmol), and a 180° needle valve and reflux condenser were attached. On the vacuum line 50 mL of toluene was added by vacuum transfer, and the reaction mixture was heated to reflux for 2 days. The toluene was removed in vacuo leaving a yellow solid. In air, about 50 mL of CH$_2$Cl$_2$ was added along with 20 mL of 4 M HCl. The CH$_2$Cl$_2$ layer was separated and combined with the 15 mL extracts of the aqueous layer. The CH$_2$Cl$_2$ solution was dried over MgSO$_4$ and filtered. Crystallization from CH$_2$Cl$_2$/hexanes afforded Cp*(η^5-C$_5$HMe$_4$)ZrCl$_2$ in 82.1% yield (3.10 g). Anal. Calcd for C$_{19}$H$_{28}$Zr$_1$Cl$_2$: C, 54.52; H, 6.74. Found: C, 54.68; H, 6.76. ^{1}H NMR (benzene-*d*$_6$): $\delta = 1.85$ (s, 15H, Cp*), 1.65 (s, 6H, C$_5$*Me*$_4$H), 2.03 (s, 6H, C$_5$*Me*$_4$H), 5.14 (s, 1H, C$_5$Me$_4$*H*). ^{13}C NMR (benzene-*d*$_6$): $\delta = 12.83$ (*C*$_5$Me$_5$), 110.45 (C$_5$*Me*$_5$), 12.98, 12.39 (C$_5$*Me*$_4$H), 119.32, 123.42, 132.40 (*C*$_5$Me$_4$H).

Cp*(C$_5$HMe$_4$)ZrMe$_2$. This compound was prepared in the same manner as Cp*(η^5-C$_5$H$_4$-CMe$_3$)ZrMe$_2$ with 2.00 g of Cp*(η^5-C$_5$HMe$_4$)ZrCl$_2$ (4.78 mmol) and 7.50 mL of 1.4 M MeLi (10.5 mmol). Drying the solid in vacuo affords Cp*(η^5-C$_5$HMe$_4$)ZrMe$_2$ in 79.3% yield (1.43 g). Anal. Calcd for C$_{21}$H$_{34}$Zr$_1$: C, 66.78; H, 9.07. Found: C, 66.68; H, 9.36. ^{1}H NMR (benzene-*d*$_6$): $\delta =$ 1.78 (s, 15 H, Cp*), -0.56 (s, 6H, Zr-C*H*$_3$) 1.57 (s, 1H, C$_5$Me$_4$*H*), 1.96 (s, 6H, C$_5$*Me*$_4$H), 4.45 (s, 6H, C$_5$*Me*$_4$H). ^{13}C NMR (benzene-*d*$_6$): $\delta = 12.10$ (*C*$_5$Me$_5$), 104.96 (C$_5$*Me*$_5$), 12.71, 12.08 (C$_5$*Me*$_4$H), 35.74 (Zr$-$*C*H$_3$), 117.13, 116.42, 123.39(*C*$_5$Me$_4$H).

Cp*(η^5-C$_5$HMe$_4$)ZrH$_2$ (15). This compound was prepared in the same manner as **8** with 1.40 g of Cp*(η^5-C$_5$HMe$_4$)ZrMe$_2$ (3.71 mmol). Recrystallization from cold petroleum ether affords Cp*(η^5-C$_5$HMe$_4$)ZrH$_2$ in 76.9% yield (1.00 g). Anal. Calcd for C$_{19}$H$_{30}$Zr: C, 65.26; H, 8.65. Found: C, 65.44; H, 9.09. ^{1}H NMR (benzene-*d*$_6$): $\delta = 1.99$ (s, 15H, Cp*), 1.81 (s, 6H, C$_5$*Me*$_4$H), 2.45 (s, 6H, C$_5$*Me*$_4$H), 7.45 (s, 2H, Zr-*H*), 4.49 (s, 1H, C$_5$Me$_4$*H*). ^{13}C NMR (benzene-*d*$_6$): $\delta = 13.02$ (*C*$_5$Me$_5$), 106.15 (C$_5$*Me*$_5$), 13.38, 14.37 (C$_5$*Me*$_4$H), 118.75, 119.18, 125.47 (*C*$_5$Me$_4$H).

{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}$_2$ZrCl$_2$ (6). In a drybox, a 100 mL round-bottom flask was charged with [Li(DME)][C$_5$H$_3$-1,3-(CMe$_3$)$_2$] (5.00 g, 18.13 mmol) and ZrCl$_4$ (2.11 g, 9.07 mmol). A reflux condenser and a 180° needle valve were attached. Via cannula, 50 mL of toluene was added to the reaction flask. The reaction mixture was heated to reflux forming a yellow solution. After 3 days, the toluene was removed in vacuo leaving a yellow/orange solid. In air, CH$_2$Cl$_2$ ($\sim$50 mL) was added along with 25 mL of 4 M HCl. The organic layer was collected, and the aqueous layer was washed with 10 mL portions of CH$_2$Cl$_2$. The combined organic layers were dried over MgSO$_4$ and filtered. The solvent was removed, leaving a yellow solid. The material was further purified by sublimation at 160 °C and 10^{-4} Torr yielding 3.10 g (66.70%) of a white solid. Anal. Calcd for C$_{26}$H$_{42}$Zr$_1$Cl$_2$: C, 60.43; H, 8.19. Found: C, 60.74; H, 8.41. ^{1}H NMR (benzene-*d*$_6$): $\delta = 1.30$ (s, 18H, C$_5$H$_3$-(C*Me*$_3$)$_2$), 5.83 (m, 2H, C$_5$*H*$_3$-(CMe$_3$)$_2$), 6.62 (m, 1H, C$_5$*H*$_3$-(CMe$_3$)$_2$). ^{13}C NMR (benzene-*d*$_6$): δ =31.61 (C$_5$H$_3$-(C*Me*$_3$)$_2$), 145.09 (C$_5$H$_3$-(*C*Me$_3$)$_2$), 105.88, 118.79, 123.31 (*C*$_5$H$_3$-(CMe$_3$)$_2$).

{η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}$_2$ZrMe$_2$. A medium frit assembly was charged with {η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}$_2$ZrCl$_2$ and evacuated. Diethyl ether (15 mL) was added by vacuum transfer. Against an Ar counterflow at -80 °C, 1.4 M MeLi in Et$_2$O was added via syringe. The reaction mixture was slowly warmed to room temperature with stirring. After 36 h of stirring, Et$_2$O was removed in vacuo and replaced with toluene. The toluene solution was filtered away from white precipitate. The precipitate was washed three times with toluene on the frit. The toluene was removed in vacuo, and the product was recrystallized from cold petroleum ether affording 1.20 g (65.1%) of {η^5-C$_5$H$_3$-1,3-(CMe$_3$)$_2$}$_2$ZrMe$_2$. Anal. Calcd for C$_{28}$H$_{48}$Zr$_1$: C, 70.67; H, 10.17. Found: C, 70.75; H, 10. 57. ^{1}H NMR (benzene-*d*$_6$): $\delta = 1.28$ (s, 18H, C$_5$H$_3$-(C*Me*$_3$)$_2$), 5.41 (m, 2H, C$_5$*H*$_3$-(CMe$_3$)$_2$), 6.55 (m, 1H, C$_5$*H*$_3$-(CMe$_3$)$_2$), 0.17 (s, 3H, Zr-C*H*$_3$). ^{13}C NMR (benzene-*d*$_6$): $\delta = 32.02$ (C$_5$H$_3$-(C*Me*$_3$)$_2$), 139.14 (C$_5$H$_3$-(*C*Me$_3$)$_2$), 34.08 (Zr-*C*H$_3$) 101.32, 106.50, 116.12 (*C*$_5$H$_3$-(CMe$_3$)$_2$).

$\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrH_2$ (13). This compound was prepared in the same manner as **8** with 1.06 g of $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrMe_2$ (2.44 mmol). After 5 days, the material was transferred into a frit assembly, and the resulting white solid was filtered and dried in vacuo yielding 0.650 g (65.0%) of $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CMe_3)_2\}_2ZrH_2$. Anal. Calcd for $C_{26}H_{42}Zr$: C, 69.73; H, 9.90. Found: C, 69.58; H, 10.06. ^1H NMR (benzene-d_6): $\delta = 1.26$ (s, 18H, $C_5H_3\text{-}(CMe_3)_2$), 5.34 (m, 2H, $C_5H_3\text{-}(CMe_3)_2$), 6.94 (m, 1H, $C_5H_3\text{-}(CMe_3)_2$), 7.36 (s, 2H, Zr-*H*). ^{13}C NMR (benzene-d_6): $\delta = 32.11$ ($C_5H_3\text{-}(CMe_3)_2$), 142.19 ($C_5H_3\text{-}(CMe_3)_2$), 100.40, 105.75, not located ($C_5H_3\text{-}(CMe_3)_2$).

$\{\eta^5\text{-}C_5H_3\text{-}1,3(CHMe_2)_2\}_2ZrCl_2$ (7). In the drybox, a 250 mL round-bottom flask was charged with $Li_2[C_5H_3\text{-}1,3(CHMe_2)_2]$ (5.10 g, 34.29 mmol) and $ZrCl_4$ (3.99 g, 17.14 mmol). A reflux condenser and a 180° needle valve were attached. Via cannula, 100 mL of toluene was added to the reaction flask. The reaction mixture was heated to reflux, forming a yellow solution. After 3 days, the toluene was removed in vacuo leaving a tan powder. In air the solid was transferred into a sublimator, and the material sublimed at 160 °C and 10^{-4} Torr, yielding 5.30 g (69.4%). Anal. Calcd for $C_{22}H_{34}Zr_1Cl_2$: C, 57.36; H, 7.44. Found: C, 57.20; H, 7.31. ^1H NMR (benzene-d_6): $\delta = 1.04$ (d, 12H, $CHMe_2$), 1.17 (d, 12H, $CHMe_2$), 3.11 (sept, 4H, $CHMe_2$), 5.62 (d, 2H, $C_5H_3\text{-}(CHMe_2)_2$), 6.26 (t, 1H, $C_5H_3\text{-}(1,3\text{-}CHMe_2)_2$). ^{13}C NMR (benzene-d_6): 23.61 ($CHMe_2$), 23.81 ($CHMe_2$), 29.74 ($CHMe_2$), 107.53, 116.49, 142.29 ($C_5H_3\text{-}(1,3\text{-}CHMe_2)_2$).

$\{\eta^5\text{-}C_5H_3\text{-}1,3(CHMe_2)_2\}_2ZrMe_2$. A medium frit assembly was charged with $\{\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}_2ZrCl_2$ (2.00 g, 4.49 mmol) and evacuated. Diethyl ether (25 mL) was added by vacuum transfer. Against an Ar counterflow at −80 °C, 1.4 M MeLi (7.1 mL, 9.9 mmol) in Et_2O was added via syringe. The reaction mixture was slowly warmed to room temperature with stirring. After 16 h of stirring, Et_2O was removed in vacuo and replaced with toluene. The toluene solution was filtered away from the white precipitate. The precipitate was washed three times with toluene on the frit. The toluene was removed in vacuo, and the product was recrystallized from cold petroleum ether, affording 1.60 g (88.1%) of $\{\eta^5\text{-}C_5H_3\text{-}1,3(CHMe_2)_2\}_2ZrMe_2$. Anal. Calcd for $C_{24}H_{40}Zr_1$: C, 68.67; H, 9.60. Found: C, 68.49; H, 9.46. ^1H NMR (benzene-d_6): $\delta = 1.10$ (d, 12H, $CHMe_2$), 1.20 (d, 12H, $CHMe_2$), −0.11 (s, 6H, Zr-CH_3), 2.74 (sept, 4H, $CHMe_2$), 5.38 (d, 2H, $C_5H_3\text{-}(CHMe_2)_2$), 6.08 (t, 1H, $C_5H_3\text{-}(1,3\text{-}CHMe_2)_2$. ^{13}C NMR (benzene-d_6): 24.12 ($CHMe_2$), 24.44 ($CHMe_2$), 33.09 (Zr-CH_3), 29.04 ($CHMe_2$), 104.8, 110.40, 134.92($C_5H_3\text{-}(1,3\text{-}CHMe_2)_2$).

$[\{(\eta^5\text{-}C_5H_3\text{-}1,3(CHMe_2)_2\}_2ZrH_2]_2$ (14). In the drybox, a thick-walled glass reaction vessel was charged with $\{\eta^5\text{-}C_5H_3\text{-}1,3(CHMe_2)_2\}_2ZrMe_2$ (0.700 g, 1.73 mmol). On the vacuum line, the reaction vessel was degassed, and approximately 10 mL of petroleum ether was added by vacuum transfer. One atmosphere of H_2 was admitted to the reaction vessel, and the reaction mixture was stirred at room temperature, depositing a white solid. After 3 days, the material was transferred into a frit assembly, and the resulting white solid was filtered and dried in vacuo yielding 0.550 g (85.0%) of $[\{(\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(CHMe_2)_2\}_2ZrH_2]_2$. Anal. Calcd for $C_{22}H_{36}Zr_1$: C, 67.45; H, 9.26. Found: C, 67.17; H, 9.58. ^1H NMR (benzene-d_6): $\delta = 1.35$ (br s, 24H, $CHMe_2$), 3.15 (sept, 4H, $CHMe_2$), 3.85 (br s, 2H, Zr-H_t), −2.10 (br s, 2H, Zr-H_b), 5.05 (d, 2H, $C_5H_3\text{-}(CHMe_2)_2$), 5.85 (t, 1H, $C_5H_3\text{-}(1,3\text{-}CHMe_2)_2$. ^{13}C NMR (benzene-d_6): 22.71 ($CHMe_2$), 26.98 ($CHMe_2$), 30.14 ($CHMe_2$), 98.23, 99.57, 104.56 ($C_5H_3\text{-}(1,3\text{-}CHMe_2)_2$).

$(\eta^5\text{-}C_5HMe_4)_2ZrMe_2$. A medium frit assembly was charged with $(\eta^5\text{-}C_5HMe_4)_2ZrCl_2$ (2.15 g, 5.32 mmol) and evacuated. Diethyl ether (25 mL) was added by vacuum transfer. Against an Ar counterflow at −80 °C, 1.4 M MeLi (8.4 mL, 11.7 mmol) in Et_2O was added via syringe. The reaction mixture was slowly warmed to room temperature with stirring. After 12 h of stirring, the solution was filtered away from white precipitate. The precipitate was washed three times with Et_2O on the frit. The Et_2O was removed in vacuo, affording 1.93 g (94.3%) of $(\eta^5\text{-}C_5HMe_4)_2ZrMe_2$. Anal. Calcd for $C_{20}H_{32}Zr_1$: C, 66.05; H, 8.87. Found: C, 65.88; H, 9.09. ^1H NMR (benzene-d_6) $\delta = 1.68$ (s, 12H, C_5Me_4H), 1.95 (s, 12H, C_5Me_4H), −0.55 (s, 6H, Zr-CH_3), 4.72 (C_5Me_4H). ^{13}C NMR (benzene-d_6) $\delta = 12.01$, 13.50 (C_5Me_4H), 35.30 (Zr-CH_3), 105.56, 111.45, 122.29 (C_5Me_4H).

$[(\eta^5\text{-}C_5HMe_4)_2ZrH_2]_2$ (15). In the drybox, a thick-walled glass reaction vessel was charged with $(\eta^5\text{-}C_5HMe_4)_2ZrMe_2$ (1.00 g, 2.75 mmol). On the vacuum line, the reaction vessel was degassed, and approximately 25 mL of petroleum ether was added by vacuum transfer. One atmosphere of H_2 was admitted to the reaction vessel, and the reaction was stirred at room temperature. After 5 days, the material was transferred into a frit assembly, and the resulting yellow solid was washed with petroleum ether and dried in vacuo, yielding 0.800 g (86.8%) of $[(\eta^5\text{-}C_5HMe_4)_2ZrH_2]_2$. Anal. Calcd for $C_{18}H_{28}Zr_1$: C, 64.41; H, 8.40. Found: C, 64.35; H, 8.77. ^1H NMR (benzene-d_6) $\delta = 2.02$ (s, 12H, C_5Me_4H), 2.14 (s, 12H, C_5Me_4H), 2.08 (br s, 2H, Zr-H_2), 45.56 (C_5Me_4H). ^{13}C NMR (benzene-d_6) $\delta = 13.36$, 15.13 (C_5Me_4H), 108.39, 111.86, 115.41 (C_5Me_4H).

Deuteration Experiments. In a typical experiment, a J. Young NMR tube is charged with 5 mg of the dihydride complex dissolved in 0.5 mL of benzene-d_6 in the drybox. On the vacuum line, the tube was frozen in liquid nitrogen and degassed using three freeze−pump−thaw cycles. While immersed in liquid nitrogen, 1 atm of deuterium gas was admitted to the tube. The solution was then thawed rapidly in a water bath, and the tube rotated at room temperature to ensure thorough mixing.

Structure Determination for 1, 3, and 6. For all samples: (1) Suitable fragments were cut from single crystals, attached to a glass fiber, and centered on an Enraf−Nonius CAD-4 diffractometer under a stream of N_2 gas at 85 K. (2) Unit cell parameters were obtained from the setting angles of 25 high angle reflections. (3) Two equivalent data sets were collected and merged in the appropriate point group. (4) Three reference reflections were measured every hour during data collection to monitor crystal decay. (5) Lorentz and polarization corrections were applied. The data for **1** and **6** were corrected for decay of 0.32% and 0.19%, respectively. An absorption correction was made for **6**. The structures of **1** and **6** were solved by Direct Methods, and that of **3** was solved by the Patterson method. For 1, 3, and 6, difference Fourier maps were used to located all missing atoms, including hydrogens. All hydrogen atoms were refined without restraints. For **1**, 2439 data were refined to R=0.015 (GOF=1.66); for **3**, 2546 data were refined to $R = 0.029$ (GOF = 1.83) and for **6**, 2330 data were refined to $R = 0.044$ (GOF = 2.04).

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Supporting Information Available: ORTEP drawings showing the complete atom labeling schemes, cell and crystal packing diagrams, tables of atomic coordinates, complete bond distances and angles, and anistropic displacement parameters for complexes **1**, **3**, **6**, and $Cp^*{}_2HfH_2$ (36 pages).[29] Internet access information is given on any current masthead page.

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(29) Crystallographic data have been deposited at CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. and copies can be obtained on request, free of charge, by quoting the publication citation; the deposition number is 102518.

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